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Andriessen

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Art Unit: Unassigned

Examiner: Unassigned

For: PROCESS FOR PREPARING A SUBSTANTIALLY
TRANSPARENT CONDUCTIVE LAYER CONFIGURATION

CLAIM OF PRIORITY

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Dear Sir:

In accordance with the provisions of 35 USC 119, Applicant claims the priority of the following application:

Application No. PCT/EP02/09427, filed in the European Patent
Office on August 22, 2002.

A certified copy of the above-listed priority document is enclosed.

Respectfully submitted,

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Date: November 6, 2003

CERTIFICATE OF MAILING

I hereby certify that this CLAIM OF PRIORITY (along with any documents referred to as being attached or enclosed) is being deposited with the United States Postal Service on the date shown below with sufficient postage as first class mail in an envelope addressed to: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.

Date: _____

11/6/03

Priority Claim (Revised 5/20/03)



Bescheinigung

Die angehefteten Unterlagen stimmen mit der ursprünglich eingereichten Fassung der auf dem nächsten Blatt bezeichneten internationalen Patentanmeldung überein.

Certificate

The attached documents are exact copies of the international patent application described on the following page, as originally filed.

Attestation

Les documents fixés à cette attestation sont conformes à la version initialement déposée de la demande de brevet international spécifiée à la page suivante.

Den Haag, den
The Hague,
La Haye, le

17. 10. 2003

Der Präsident des Europäischen Patentamts
Im Auftrag
For the President of the European Patent Office
Le Président de l'Office européen des brevets
p. o.

G. KOESTEL

Patentanmeldung Nr.
Patent application n°
Demande de brevet n°

PCT/EP 02/09427

Blatt 2 der Bescheinigung
Sheet 2 of the certificate
Page 2 de l'attestation



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Application no.:
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Titre de l'invention:

Anmeldetag:
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V	Designation of States	
V-1	Regional Patent (other kinds of protection or treatment, if any, are specified between parentheses after the designation(s) concerned)	AP: GH GM KE LS MW MZ SD SL SZ TZ UG ZM ZW and any other State which is a Contracting State of the Harare Protocol and of the PCT EA: AM AZ BY KG KZ MD RU TJ TM and any other State which is a Contracting State of the Eurasian Patent Convention and of the PCT EP: AT BE BG CH&LI CY CZ DE DK EE ES FI FR GB GR IE IT LU MC NL PT SE SK TR and any other State which is a Contracting State of the European Patent Convention and of the PCT OA: BF BJ CF CG CI CM GA GN GQ GW ML MR NE SN TD TG and any other State which is a member State of OAPI and a Contracting State of the PCT
V-2	National Patent (other kinds of protection or treatment, if any, are specified between parentheses after the designation(s) concerned)	AE AG AL AM AT AU AZ BA BB BG BR BY BZ CA CH&LI CN CO CR CU CZ DE DK DM DZ EC EE ES FI GB GD GE GH GM HR HU ID IL IN IS JP KE KG KP KR KZ LC LK LR LS LT LU LV MA MD MG MK MN MW MX MZ NO NZ OM PH PL PT RO RU SD SE SG SI SK SL TJ TM TN TR TT TZ UA UG US UZ VC VN YU ZA ZM ZW

PROCESS FOR PREPARING A SUBSTANTIALLY TRANSPARENT CONDUCTIVE LAYER

Field of the invention

5 The present invention relates to a single layer composite substantially transparent conductive layer.

Background of the invention.

10 In many applications there is a requirement for inexpensive transparent conducting layers, but a busbar will be also required for some of the (large area) applications. Highly conductive (non-transparent) patterns can be made by screen-printing conducting pastes such as silver or carbon black pastes. Vacuum evaporation of
15 metals through shadow masks is another method. Yet another method makes use of homogeneous conductive metallized surfaces which can be patterned by use of photoresist technology in combination with a metal etching agent. Photographic films can, under certain conditions, be used for making electrically conductive silver
20 "images".

US 3,664,837 describes the use of light sensitive evaporated silver halide film which upon exposure and after development results in conductive images. DE 1,938,373 describes a photographic method for producing conducting paths, resistances and capacitors
25 for microcircuits starting from coated silver halide emulsions. US 3,600,185 describes the production of electrically conductive patterns by means of diffusion transfer techniques.

Combinations of a transparent polymer-based conductor and a high conductive (non-transparent) pattern are described in some
30 publications. DE-A 196 27 071 discloses an electroluminescent configuration, which contains hole and/or electron injecting layers, wherein the polymeric organic conductor is selected from the group of polyfurans, polypyrroles, polyanilines, polythiophenes and polypyridines. DE-A 196 27 071 also discloses the use of
35 poly(3,4-ethylenedioxythiophene) as a charge-injection layer on transparent metallic electrodes such as ITO (indium-tin oxide) and that the following materials are suitable as transparent and conductive materials: a) metal oxides e.g. ITO, tin oxide etc.; b) semi-transparent metal films e.g. Au, Pt, Ag, Cu etc. The latter
40 being applied by vacuum techniques.

EP-A 510 541 discloses an organic electroluminescent device having an anode, an organic hole injection transport layer, an

organic luminescent layer and a cathode formed sequentially in this order, wherein the organic hole injection transport layer contains a metal complex and/or a metal salt of an aromatic carboxylic acid. EP-A 510 541 further discloses that the conductive layers used in
5 such devices may have a multi-layer structure by depositing different types of conductive materials selected from a metal, e.g. Al, Au, Ag, Ni, Pd or Te, a metal oxide, carbon black or a conductive resin such as poly(3-methylthiophene), but no specific combinations are exemplified.

10 US 5,447,824 discloses a method of manufacturing a pattern of an electrically conductive polymer on a substrate surface, said method comprising: a) forming a liquid layer on a surface of said substrate from a solution containing a material capable of forming
15 said electrically conductive polymer upon being heated, e.g. 3,4-ethylenedioxythiophene, an oxidizing agent and a base, b) exposing said liquid layer to patterned radiation, and c) heating said layer thereby forming a pattern of an electrically conductive polymer, said conductive polymer being formed in unexposed areas and a non-conductive polymer being formed in the exposed areas of the layer.
20 The galvanic provision of the conductive polymer pattern with a metal layer, e.g. silver, copper, nickel or chromium, is also disclosed in US 5,447,824.

WO 98/54767 discloses a conductive layer system, particularly for a transparent or semi-transparent electrode or
25 electroluminescent configuration, comprising at least two layers, characterized in that the first layer contains an organic or organometallic electrically conductive polymer, which is transparent or semi-transparent in the visible range of the electromagnetic spectrum, e.g. a polymer selected from the group
30 consisting of polythiophene, polypyrrole, polyaniline, polyacetylene or their optionally substituted derivatives and the second layer contains at least one electrically conductive inorganic compound or a metal or an appropriately doped semi-metal e.g. a material selected from the group consisting of Cu, Ag, Au,
35 Pt, Pd, Fe, Cr, Sn, Al or their alloys or conductive carbon. In a preferred embodiment the second layer is a conductive pattern formed by an open grid structure, preferably with a 5-500 μm grid so that it cannot be perceived by the human eye. Invention example 2 discloses a poly(3,4-ethylenedioxythiophene) [PEDOT]/poly(styrene
40 sulphonate) [PSS] layer with a surface resistivity of 1500 Ω/square to which conducting tracks of "Leitsilber" (a silver particle dispersion) ca. 2 mm wide had been applied by a printing technique.

The layer configuration disclosed in Example 2 of WO 98/54767 has the disadvantages of the grid of "Leitsilber" requiring a thickness of 5 to 10 μm to realize layers with a surface resistance of 0.5 to 1 Ω/square , which means that the surface of the configuration will have a certain roughness which will limit its applications, making it difficult to apply a thin, e.g. 100 nm, functional layer. Furthermore, an aqueous PEDOT/PSS dispersion would not wet such a "Leitsilber" grid and hence a usable multilayer conductive configuration would not result.

Moreover, with an intrinsically conductive polymer layer or a metal grid outermost wetting problems arise as regards coating of thin functional layers. Furthermore, for devices requiring very thin functional layers such as transistors, the thickness of a multilayer electrode and even slight deviations from flatness are disadvantageous in their production.

Aspects of the invention.

It is therefore an aspect of the present invention to provide a conductive electrode with similar properties, but thinner than multilayer electrodes comprising a conductive polymer layer and a conductive metal layer with an outermost layer with improved flatness.

It is a further aspect of the present invention to provide a process for preparing a conductive electrode with similar properties, but thinner than multilayer electrodes comprising a conductive polymer layer and a conductive metal layer with an outermost layer with improved flatness.

It is also an aspect of the present invention to prevent ion migration from the conductive electrode.

Further aspects and advantages of the invention will become apparent from the description hereinafter.

Summary of the invention.

35

It has been surprisingly found that a thin substantially transparent conductive layer with high conductivity and with an outermost surface with improved flatness can be realized in a layer containing an intrinsically conductive polymer, e.g. PEDOT/PSS, and a conductive metal, e.g. silver, non-uniformly distributed therein to which functional layers can be readily applied.

Upon applying a potential between the conductive layer, according to the present invention, as cathode and a counter-electrode as cathode under conditions of high relative humidity metal ions present at the anode, there always being an equilibrium
5 between metal ions and metal atoms, diffuse under the applied potential to the cathode, where they are deposited at metal atoms which stack forming dendritic metal which grow towards the anode. This results long term in short circuiting of the electrodes.

In the case of conductive layers containing silver ions
10 migrate and silver dendrites are formed. The use of benzotriazole as a silver electrode-stabilizer is disclosed in US 4,821,148 and US 6,174,606 and Evenpoel et al. in 1970 disclosed the use of thiourea in Metallurgie X, volume 4, page 132, and Ambland et al. in 1978 disclosed the use of tartaric acid in Surface Technology,
15 volume 6, pages 409-423. However, these remedies were unsuccessful with the conductive layer of the present invention. Surprisingly, it has been found that particular phenyl-mercaptotetrazole compounds are capable of substantially preventing the formation of silver dendrites.

20 Aspects of the present invention are realized by a substantially transparent conductive layer on a support, the layer comprising an intrinsically conductive polymer and a conductive metal non-uniformly distributed therein and forming of itself a conductive entity.

25 Aspects of the present invention are also realized by a process for preparing a substantially transparent conductive layer on a support, the layer comprising an intrinsically conductive polymer and a conductive metal non-uniformly distributed therein and forming of itself a conductive entity, comprising the step of:
30 preparing the non-uniformly distributed conductive metal by a photographic process.

Aspects of the present invention are also realized by a light emitting diode comprising the above-described conductive layer or produced according to the above-described process.

35 Aspects of the present invention are also realized by a photovoltaic device comprising the above-described conductive layer or produced according to the above-described process.

Aspects of the present invention are also realized by a transistor comprising the above-described conductive layer or
40 produced according to the above-described process.

Aspects of the present invention are also realized by an electroluminescent device comprising the above-described conductive layer or produced according to the above-described process.

Preferred embodiments are disclosed in the dependent claims.

5

Detailed description of the invention.

Figure 1 shows four silver patterns, pattern (a) representing a continuous silver layer $3 \times 3 \text{ cm}^2$ in area, pattern (b) representing
10 a regular strip pattern, the parallel strips being 10 mm apart and having a width of 1 mm; pattern (c) representing a regular strip pattern, the parallel strips being 5 mm apart and having a width of 150 μm ; and pattern (d) representing no silver development.

15

Definitions

The term alkyl means all variants possible for each number of carbon atoms in the alkyl group i.e. for three carbon atoms: n-propyl and isopropyl; for four carbon atoms: n-butyl, isobutyl, and
20 tertiary-butyl; for five carbon atoms: n-pentyl, 1,1-dimethylpropyl, 2,2-dimethylpropyl and 2-methyl-butyl etc.

The term aqueous for the purposes of the present invention means containing at least 60% by volume of water, preferably at least 80% by volume of water, and optionally containing water-
25 miscible organic solvents such as alcohols e.g. methanol, ethanol, 2-propanol, butanol, iso-amyl alcohol, octanol, cetyl alcohol etc.; glycols e.g. ethylene glycol; glycerine; N-methyl pyrrolidone; methoxypropanol; and ketones e.g. 2-propanone and 2-butanone etc.

The term "support" means a "self-supporting material" so as to
30 distinguish it from a "layer" which may be coated on a support, but which is itself not self-supporting. It also includes any treatment necessary for, or layer applied to aid, adhesion to the support.

The term continuous layer refers to a layer in a single plane
35 covering the whole area of the support and not necessarily in direct contact with the support.

The term non-continuous layer refers to a layer in a single plane not covering the whole area of the support and not necessarily in direct contact with the support.

40 The term coating is used as a generic term including all means of applying a layer including all techniques for producing continuous layers, such as curtain coating and doctor-blade coating

and all techniques for producing non-continuous layers such as screen printing, ink jet printing, flexographic printing, and techniques for producing continuous layers

The term intrinsically conductive polymer means organic polymers which have (poly)-conjugated π -electron systems (e.g. double bonds, aromatic or heteroaromatic rings or triple bonds) and whose conductive properties are not influenced by environmental factors such as relative humidity.

The term "conductive" is related to the electric resistance of the material. The electric resistance of a layer is generally expressed in terms of surface resistance R_s (often specified as Ω/square). Alternatively, the conductivity may be expressed in terms of volume resistivity $R_v = R_s \cdot d$, wherein d is the thickness of the layer, volume conductivity $k_v = 1/R_v$ [unit: S(iemens)/cm] or surface conductance $k_s = 1/R_s$ [unit: S(iemens).square].

The term photographic refers to any photochemical process particularly those based on silver halide processes.

The term silver salt diffusion transfer process refers to a process developed independently by A. Rott [GB 614,155 and Sci. Photogr., (2)13, 151 (1942)] and E. Weyde [DE 973,769] and described by G. I. P. Levenson in Chapter 16 of "The Theory of the Photographic Process Fourth Edition", edited by T. H. James, pages 466 to 480, Eastman Kodak Company, Rochester (1977).

The term substantially transparent means that the integral transmission of visible light is above 50% of the incident light normal to the conductive layer of the present invention i.e. the layer had an overall optical density of less than 0.30, although local transmission of visible light through the lines of the silver pattern may be well below 10% of the incident light normal to the conductive layer of the present invention i.e. well above an optical density of 1.0.

The abbreviation PEDOT represents poly(3,4-ethylenedioxythiophene).

The abbreviation PSS represents poly(styrene sulphononic acid) or poly(styrenesulphonate).

Conducting layer

Aspects of the present invention are realized by a substantially transparent conductive layer on a support, the layer comprising an intrinsically conductive polymer and a conductive

metal non-uniformly distributed therein and forming of itself a conductive entity.

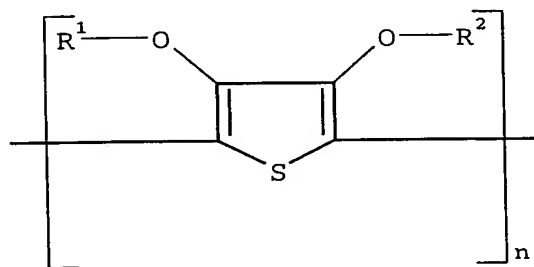
According to a first embodiment of the conducting layer, according to the present invention, the conductive metal is silver.

intrinsically conductive polymer

5

The intrinsically conductive polymers used in the present invention can be any intrinsically conductive polymer known in the art e.g. polyacetylene, polypyrrole, polyaniline, polythiophene, etc. Details about suitable intrinsically conductive polymers can
10 be found in textbooks, such as "Advances in Synthetic Metals", ed. P. Bernier, S. Lefrant, and G. Bidan, Elsevier, 1999; "Intrinsically Conducting Polymers: An Emerging Technology", Kluwer (1993); "Conducting Polymer Fundamentals and Applications, A Practical Approach", P. Chandrasekhar, Kluwer, 1999; and "Handbook
15 of Organic Conducting Molecules and Polymers", Ed. Walwa, Vol. 1-4, Marcel Dekker Inc. (1997).

According to a second embodiment of the conductive layer process, according to the present invention, the intrinsically conductive polymer contains structural units represented by formula
20 (I):



(I)

in which, each of R^1 and R^2 independently represents hydrogen or a C_{1-4} alkyl group or together represent an optionally substituted C_{1-4} alkylene group or a cycloalkylene group.

25 According to a third embodiment of the conductive layer, according to the present invention, the intrinsically conductive polymer is a polymer or copolymer of a 3,4-dialkoxythiophene in which the two alkoxy groups together represent an optionally substituted oxy-alkylene-oxy bridge.

30 According to a fourth embodiment of the conductive layer, according to the present invention, the intrinsically conductive polymer is a polymer or copolymer of a 3,4-dialkoxy-thiophenes in which the two alkoxy groups together represent an optionally

substituted oxy-alkylene-oxy bridge and is selected from the group consisting of: poly(3,4-methylenedioxythiophene), poly(3,4-methylenedioxythiophene) derivatives, poly(3,4-ethylenedioxythiophene), poly(3,4-ethylenedioxythiophene) derivatives, poly(3,4-propylenedioxythiophene), poly(3,4-propylenedioxythiophene) derivatives, poly(3,4-butylenedioxythiophene) and poly(3,4-butylenedioxythiophene) derivatives and copolymers thereof.

According to a fifth embodiment of the conductive layer, according to the present invention, the intrinsically conductive polymer is a polymer or copolymer of a 3,4-dialkoxy-thiophenes in which the two alkoxy groups together represent an optionally substituted oxy-alkylene-oxy bridge and the substituents for the oxy-alkylene-oxy bridge are alkyl, alkoxy, alkyloxyalkyl, carboxy, alkylsulfonato and carboxy ester groups.

According to a sixth embodiment of the conductive layer, according to the present invention, the intrinsically conductive polymer is a polymer or copolymer of a 3,4-dialkoxy-thiophenes in which the two alkoxy groups together represent an optionally substituted oxy-alkylene-oxy bridge and the two alkoxy groups together represent an optionally substituted oxy-alkylene-oxy bridge which is a 1,2-ethylene group, an optionally alkyl-substituted methylene group, an optionally C₁₋₁₂-alkyl- or phenyl-substituted 1,2-ethylene group, a 1,3-propylene group or a 1,2-cyclohexylene group.

Such polymers are disclosed in Handbook of Oligo- and Polythiophenes Edited by D. Fichou, Wiley-VCH, Weinheim (1999); by L. Groenendaal et al. in Advanced Materials, volume 12, pages 481-494 (2000); L. J. Kloeppner et al. in Polymer Preprints, volume 40(2), page 792 (1999); P. Schottland et al. in Synthetic Metals, volume 101, pages 7-8 (1999); and D. M. Welsh et al. in Polymer Preprints, volume 38(2), page 320 (1997).

Organic polymer containing structural units according to formula (I) can be polymerized chemically or electrochemically. Chemical polymerization can be carried out oxidatively or reductively. The oxidation agents used for the oxidative polymerisation of pyrrole, such as described for example in J. Amer. Chem. Soc., vol. 85, pages 454-458 (1963) and J. Polym. Sci. Part A Polymer Chemistry, volume 26, pages 1287-1294 (1988), can be utilized for the oxidative polymerization of thiophenes. According to a seventh embodiment of the present invention, the inexpensive and easily accessible oxidation agents such as iron(III) salts such as FeCl₃, the iron(III) salts of organic acids, e.g. Fe(OTs)₃, H₂O₂,

$K_2Cr_2O_7$, alkali and ammonium persulphates, alkali perborates and potassium permanganate are used in the oxidative polymerization.

Theoretically the oxidative polymerization of thiophenes requires 2.25 equivalents of oxidation agent per mole thiophene of formula (I) [see e.g. J. Polymer Science Part A Polymer Chemistry, volume 26, pages 1287-1294 (1988)]. In practice an excess of 0.1 to 2 equivalents of oxidation agent is used per polymerizable unit. The use of persulphates and iron(III) salts has the great technical advantage that they do not act corrosively. Furthermore, in the presence of particular additives oxidative polymerization of the thiophene compounds according to formula (I) proceeds so slowly that the thiophenes and oxidation agent can be brought together as a solution or paste and applied to the substrate to be treated. After application of such solutions or pastes the oxidative polymerization can be accelerated by heating the coated substrate as disclosed in US 6,001,281 and WO 00/14139 herein incorporated by reference.

Reductive polymerization can be performed using the Stille (organotin) or Suzuki (organoboron) routes described in 2002 by Apperloo et al. in Chem. Eur. Journal, volume 8, pages 2384-2396, and as disclosed in 2001 in Tetrahedron Letters, volume 42, pages 155-157 and in 1998 in Macromolecules, volume 31, pages 2047-2056 respectively or with nickel complexes as disclosed in 1999 in Bull. Chem. Soc. Japan, volume 72, page 621 and in 1998 in Advanced Materials, volume 10, pages 93-116.

1-phenyl-5-mercato-tetrazole compound in which the phenyl group is substituted with one or more electron accepting groups

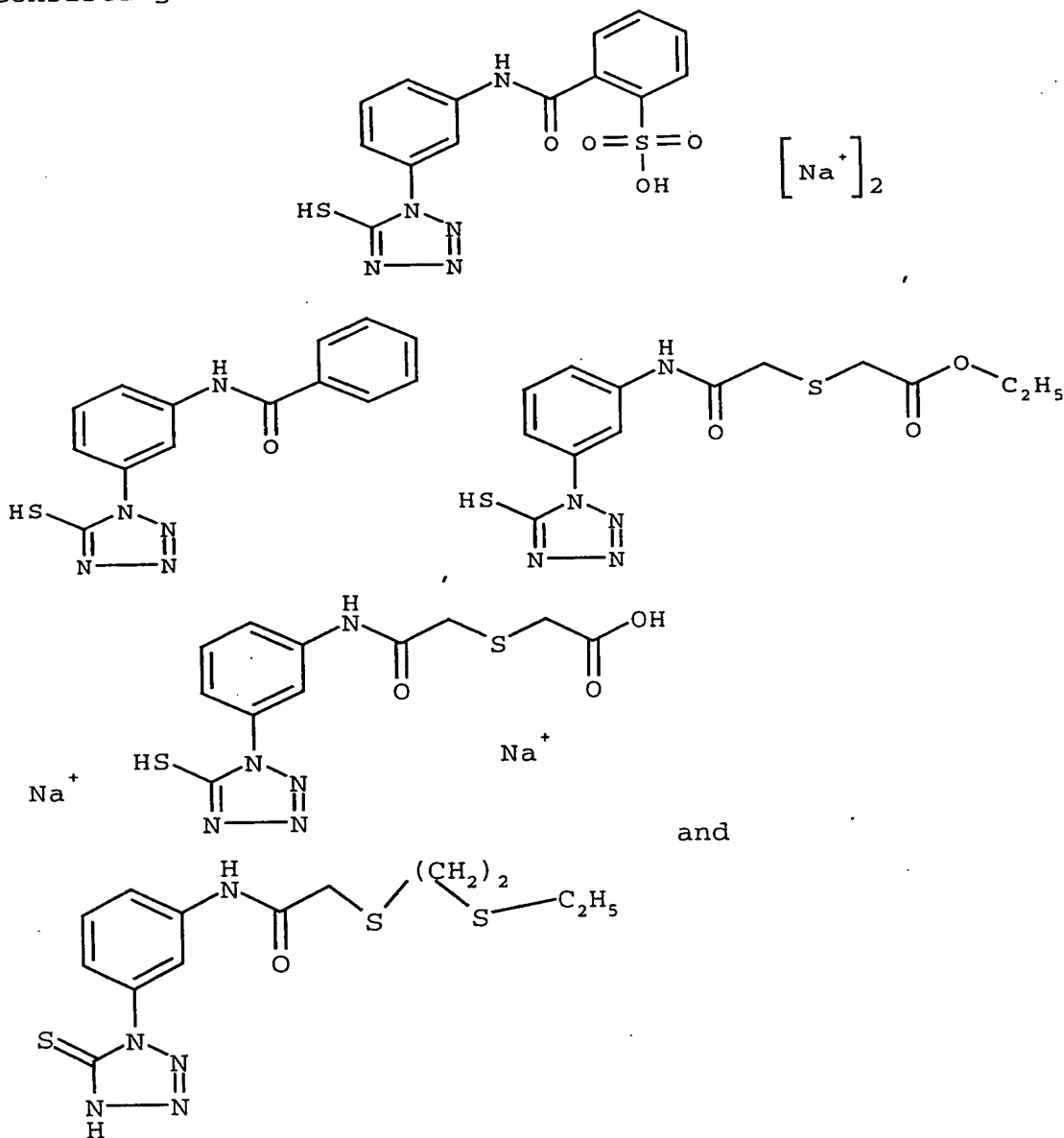
According to a seventh embodiment of the conducting layer, according to the present invention, the conductive layer further contains a silver-ion stabilizer.

According to an eighth embodiment of the conducting layer, according to the present invention, the conductive layer further contains a silver-ion stabilizer which is a 1-phenyl-5-mercato-tetrazole compound in which the phenyl group is substituted with one or more electron accepting groups.

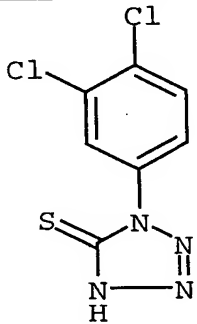
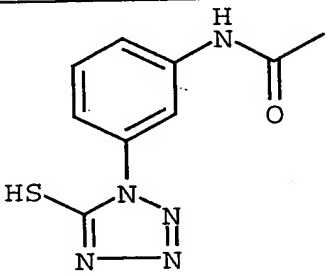
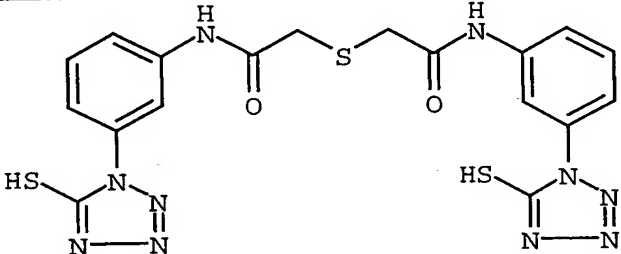
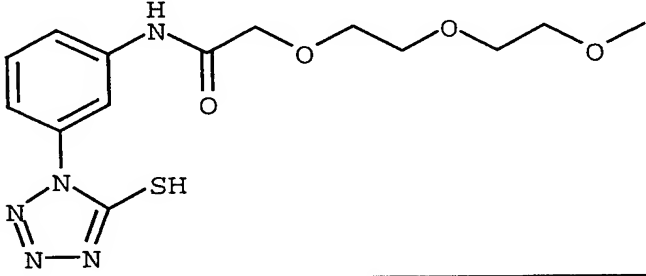
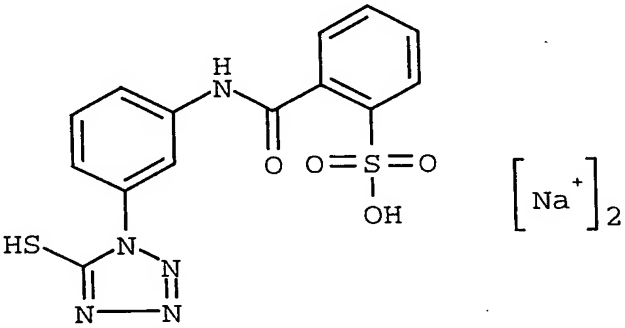
According to a ninth embodiment of the conducting layer, according to the present invention, the conductive layer further contains a silver-ion stabilizer which is a 1-phenyl-5-mercato-tetrazole compound in which the phenyl group is substituted with one or more electron accepting groups selected from the

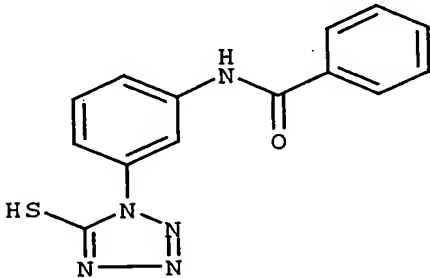
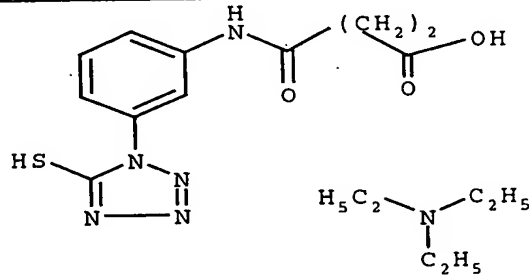
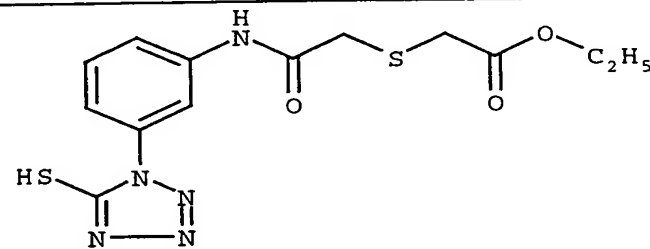
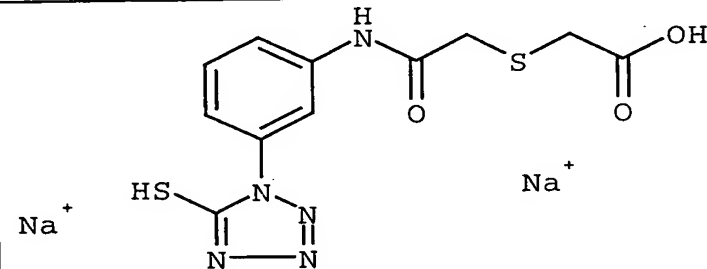
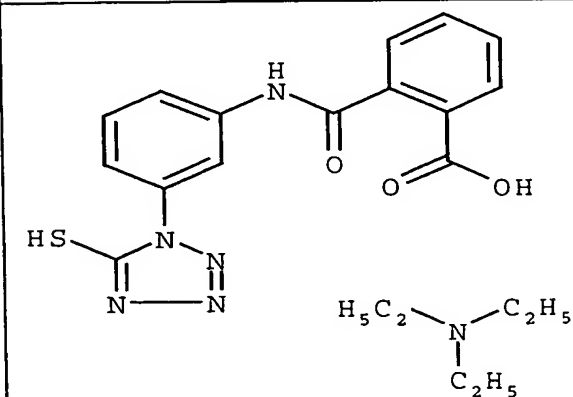
group consisting of chloride, fluoride, cyano, sulfonyl, nitro, acid amido and acylamino groups.

According to a tenth embodiment of the conducting layer, according to the present invention, the conductive layer further contains a silver-ion stabilizer which is selected from the group consisting of: 1-(3',4'-dichlorophenyl)-5-mercapto-tetrazole,



Suitable 1-phenyl-5-mercapto-tetrazole compounds with substituted phenyl groups [PMT], according to the present invention, include:

	Structural formula	
PMT01		1-(3',4'-dichlorophenyl)-5-mercapto-tetrazole
PMT02		1-(3'-acetylaminophenyl)-5-mercapto-tetrazole
PMT03		
PMT04		
PMT05		

PMT06		1-(3'-benzoylamino-phenyl)-5-mercapto-tetrazole
PMT07		
PMT08		
PMT09		
PMT10		

PMT11		
PMT12		
PMT13		
PMT14		

Process for preparing a conductive layer

Aspects of the present invention are also realized by a
 5 process for preparing a substantially transparent conductive layer
 on a support, the layer comprising an intrinsically conductive
 polymer and a conductive metal non-uniformly distributed therein
 and forming of itself a conductive entity, comprising the step of:
 preparing the non-uniformly distributed conductive metal by a
 10 photographic process.

According to a first embodiment of the process, according to the present invention, the photographic process comprises the steps of: coating the support with a layer containing the intrinsically conductive polymer and a nucleation agent; producing a non-continuous silver layer in the nucleation layer using silver salt diffusion transfer.

According to a second embodiment of the process, according to the present invention, the photographic process comprises the steps of: coating the support with a layer containing the intrinsically conductive polymer and palladium sulphide e.g. palladium sulphide nanoparticles, as a nucleation agent; producing a non-continuous silver layer in the nucleation layer using silver salt diffusion transfer.

According to a third embodiment of the process, according to the present invention, the photographic process comprises the steps of: coating the support with a layer containing an intrinsically conductive polymer, silver halide and gelatin with a weight ratio of gelatin to silver halide in the range of 0.05 to 0.3, image-wise exposing the layer, and developing the exposed layer to produce the non-uniformly distributed silver.

Surfactants

According to an eleventh embodiment of the conductive layer, according to the present invention, the conductive layer further contains a surfactant.

According to a twelfth embodiment of the conductive layer, according to the present invention, the conductive layer further contains a non-ionic surfactant e.g. ethoxylated/fluoroalkyl surfactants, polyethoxylated silicone surfactants, polysiloxane/polyether surfactants, ammonium salts of perfluoroalkylcarboxylic acids, polyethoxylated surfactants and fluorine-containing surfactants.

Suitable non-ionic surfactants include:

35

Surfactant no. 01 = ZONYL™ FSN, a 40% by weight solution of $F(CF_2CF_2)_{1-9}CH_2CH_2O(CH_2CH_2O)_xH$ in a 50% by weight solution of isopropanol in water where $x = 0$ to about 25, from DuPont;

Surfactant no. 02 = ZONYL™ FSN-100: $F(CF_2CF_2)_{1-9}CH_2CH_2O(CH_2CH_2O)_xH$ where $x = 0$ to about 25, from DuPont;

Surfactant no. 03 = ZONYL™ FS300, a 40% by weight aqueous solution

- of a fluorinated surfactant, from DuPont;
- Surfactant no. 04 = ZONYL™ FSO, a 50% by weight solution of a mixture of ethoxylated non-ionic fluoro-surfactant with the formula:

$$F(CF_2CF_2)_{1-7}CH_2CH_2O(CH_2CH_2O)_yH$$
 where $y = 0$ to ca. 15 in a 50% by weight solution of ethylene glycol in water, from DuPont;
- Surfactant no. 05 = ZONYL™ FSO-100, a mixture of ethoxylated non-ionic fluoro-surfactant from DuPont with the formula: $F(CF_2CF_2)_{1-7}CH_2CH_2O(CH_2CH_2O)_yH$ where $y = 0$ to ca. 15 from DuPont;
- Surfactant no. 06 = Tegoglide™ 410, a polysiloxane-polymer copolymer surfactant, from Goldschmidt;
- Surfactant no. 07 = Tegowet™, a polysiloxane-polyester copolymer surfactant, from Goldschmidt;
- Surfactant no. 08 = FLUORAD™FC431: $CF_3(CF_2)_7SO_2(C_2H_5)N-CH_2CO-(OCH_2CH_2)_nOH$ from 3M;
- Surfactant no. 09 = FLUORAD™FC126, a mixture of the ammonium salts of perfluorocarboxylic acids, from 3M;
- Surfactant no. 10 = Polyoxyethylene-10-lauryl ether
- Surfactant no. 11 = FLUORAD™FC430, a 98.5% active fluoroaliphatic ester from 3M;

According to a thirteenth embodiment of the conductive layer, according to the present invention, the conductive layer further contains an anionic surfactant.

5 Suitable anionic surfactants include:

- Surfactant no. 12 = ZONYL™ 7950, a fluorinated surfactant, from DuPont;
- Surfactant no. 13 = ZONYL™ FSA, 25% by weight solution of $F(CF_2CF_2)_{1-9}CH_2CH_2SCH_2CH_2COOLi$ in a 50% by weight solution of isopropanol in water, from DuPont;
- Surfactant no. 14 = ZONYL™ FSE, a 14% by weight solution of $[F(CF_2CF_2)_{1-7}CH_2CH_2O]_xP(O)(ONH_4)_y$ where $x = 1$ or 2 ; $y = 2$ or 1 ; and $x + y = 3$ in a 70% by weight aqueous ethylene glycol solution, from DuPont;
- Surfactant no. 15 = ZONYL™ FSJ, a 40% by weight solution of a blend of $F(CF_2CF_2)_{1-7}CH_2CH_2O]_xP(O)(ONH_4)_y$ where $x = 1$ or 2 ; $y = 2$ or 1 ; and $x + y = 3$ with a hydrocarbon surfactant in 25% by weight solution of isopropanol in water, from DuPont;

- Surfactant no. 16 = ZONYL™ FSP, a 35% by weight solution of
 $[F(CF_2CF_2)_{1-7}CH_2CH_2O]_xP(O)(ONH_4)_y$ where $x = 1$ or
 2 ; $y = 2$ or 1 and $x + y = 3$ in 69.2% by weight
 solution of isopropanol in water, from DuPont;
- Surfactant no. 17 = ZONYL™ UR: $[F(CF_2CF_2)_{1-7}CH_2CH_2O]_xP(O)(OH)_y$ where x
 $= 1$ or 2 ; $y = 2$ or 1 and $x + y = 3$, from DuPont;
- Surfactant no. 18 = ZONYL™ TBS: a 33% by weight solution of
 $F(CF_2CF_2)_{3-8}CH_2CH_2SO_3H$ in a 4.5% by weight
 solution of acetic acid in water, from DuPont;
- Surfactant no. 19 = ammonium salt of perfluoro-octanoic acid from 3M

Binder

According to a fourteenth embodiment of the conductive layer,
 5 according to the present invention, the conductive layer further
 contains a binder.

Crosslinking agent

10 According to a fifteenth embodiment of the conductive layer,
 according to the present invention, the conductive layer further
 contains a cross-linking agent.

Support

15 According to a sixteenth embodiment of the conductive layer,
 according to the present invention, the support is transparent or
 translucent.

According to a seventeenth embodiment of the conductive layer,
 20 according to the present invention, the support is a polymeric
 film, silicon, a ceramic, an oxide, glass, polymeric film
 reinforced glass, a glass/plastic laminate, a metal/plastic
 laminate, optionally treated paper and laminated paper.

According to an eighteenth embodiment of the conductive layer,
 25 according to the present invention, the support is provided with a
 subbing layer or other adhesion promoting means to aid adhesion to
 the substantially transparent conductive layer.

According to a nineteenth embodiment of the conductive layer,
 according to the present invention, the support is a transparent or
 30 translucent polymer film.

A transparent or translucent support suitable for use with the
 electroconductive or antistatic layers, according to the present

invention, may be rigid or flexible and consist of a glass, a glass-polymer laminate, a polymer laminate, a thermoplastic polymer or a duroplastic polymer. Examples of thin flexible supports are those made of a cellulose ester, cellulose triacetate, polypropylene, polycarbonate or polyester, with poly(ethylene terephthalate), poly(ethylene naphthalene-1,4-dicarboxylate), polystyrene, polyethersulphone, polycarbonate, polyacrylate, polyamide, polyimides, cellulose triacetate, polyolefins and poly(vinylchloride), optionally treated by corona discharge or glow discharge or provided with a subbing layer.

Electroluminescent devices

Aspects of the present invention are also realized by an electroluminescent device comprising the conductive layer, according to the present invention, or produced according to the process, according to the present invention.

Thin film electroluminescent devices (ELDs) are all characterized by one (or more) electroluminescent active layer(s) sandwiched between two electrodes. Optionally a dielectric layer may also be part of the sandwich.

Thin film ELDs can be subdivided into organic and inorganic based ELDs. Organic-based thin film ELDs can be subdivided into low molecular weight organic devices including oligomers (Organic Light Emitting Diodes (OLEDs)) and high molecular weight organic devices (Polymer Light Emitting Diodes (PLEDs)). The inorganic ELDs on the other hand can be further subdivided into the High Voltage Alternating Current (HV-AC) ELDs and the Low Voltage Direct Current (LV-DC) ELDs. The LV-DC ELDs include Powder ELDs (DC-PEL Devices or DC-PELDs) and thin film DC-ELDs, hereinafter called Inorganic Light Emitting Diodes (ILEDs).

The basic construction of organic ELDs (PLED and OLED) comprises following layer arrangement : a transparent substrate (glass or flexible plastic), a transparent conductor, e.g. Indium Tin Oxide (ITO), a hole transporting layer, a luminescent layer, and a second electrode, e.g. a Ca, Mg/Ag or Al/Li electrode. For OLEDs the hole transporting layer and the luminescent layer are 10-50 nm thick and applied by vacuum deposition, whereas for PLEDs the hole transporting layer is usually about 40 nm thick and the luminescent layer is usually about 100 nm thick and applied by spin coating or other non-vacuum coating techniques. A direct voltage of 5 - 10 V is applied between both electrodes and light emission

results from holes and electrons being injected from the positive and negative electrodes respectively combining in the luminescent layer thereby producing the energy to excite the luminescent species to emit light.

5 In OLEDs the hole transporting layer and electroluminescent layer consist of low molecular organic compounds, N,N'-diphenyl-1,1'-biphenyl-4,4'-diamine (TPD) can, for example be used as the hole transporter and aluminium (III) 8-hydroxyquinoline complex (Alq₃), polyaromatics (anthracene derivatives, perylene derivatives
10 and stilbene derivatives) and polyhetero-aromatics (oxazoles, oxadiazoles, thiazoles etc.) can be used as electroluminescent compounds.

In PLEDs electroluminescent compounds that can be used are polymers like the non-conjugated polyvinylcarbazole derivatives
15 (PVK) or conjugated polymers like poly(p-phenylene vinylenes) (PPV), polyfluorenes, poly(3-alkylthiophene), poly(p-phenylene ethynylenes) etc.

Low voltage DC PEL Devices generally comprise a transparent substrate, a transparent conductor (ITO), a doped ZnS phosphor
20 layer (20µm), and a top electrode of evaporated aluminium. The phosphor layer is applied by means of the doctor blade technique or screen printing on an ITO conducting layer. Subsequently an aluminium electrode is applied by evaporation. Upon applying a direct current voltage of several volts (ITO positive), holes start
25 moving towards the aluminium electrode, thereby creating an insulating region (about 1 µm in thickness) next to the ITO layer within one minute or so. This results in a current drop which is associated with the onset of light emission. This process has been called the forming process. In the thin high resistive phosphor
30 layer thereby formed, high electric fields occur and electroluminescence is already possible at low voltages (typically between 10 and 30 V).

In hybrid LEDs, inorganic emitting so-called quantum dots are used in combination with organic polymers with charge transporting
35 properties and in some cases also emitting properties. Hybrid LEDs with CdSe nano particles have been reported by Colvin et al. [see Nature, volume 370, pages 354-357, (1994)], Dabbousi et al. [see Appl. Phys. Lett., volume 66, pages 1316-1318 (1995), and Gao et al. [see J. Phys. Chem. B, volume 102, pages 4096-4103 (1998)],
40 herein incorporated by reference.

Light-emitting devices with ZnS:Cu nano-crystals and a non-semiconducting polymer have been reported by Huang et al. [see

Appl. Phys. Lett., volume 70, pages 2335-2337 (1997)] and Que et al. [see Appl. Phys. Lett., volume 73, pages 2727-2729 (1998)], herein incorporated by reference, with turn on voltages below 5 V.

According to a first embodiment of the electroluminescent device, according to the present invention, the electroluminescent device is a light emitting diode.

According to a second embodiment of the electroluminescent device, according to the present invention, the electroluminescent device further comprises a layer of an electroluminescent phosphor.

According to a third embodiment of the electroluminescent device, according to the present invention, the electroluminescent device comprises a layer of an electroluminescent phosphor, wherein the electroluminescent phosphor belongs to the class of II-VI semiconductors e.g. ZnS, or is a combination of group II elements with oxidic anions, the most common being silicates, phosphates, carbonates, germanates, stannates, borates, vanadates, tungstates and oxysulphates. Typical dopants are metals and all the rare earths e.g. Cu, Ag, Mn, Eu, Sm, Tb and Ce.

According to a fourth embodiment of the electroluminescent device, according to the present invention, the electroluminescent device comprises a layer of an electroluminescent phosphor, wherein the electroluminescent phosphor is encapsulated with a transparent barrier layer against moisture e.g. Al_2O_3 and AlN. Such phosphors are available from Sylvania, Shinetsu polymer KK, Durel, Acheson and Toshiba. An example of coatings with such phosphors is 72X, available from Sylvania/GTE, and coatings disclosed in US 4,855,189.

According to a fifth embodiment of the electroluminescent device, according to the present invention, the electroluminescent device further comprises a layer of an electroluminescent phosphor, wherein the electroluminescent phosphor is ZnS doped with manganese, copper or terbium, or CaGa_2S_4 doped with cerium e.g. the electroluminescent phosphor pastes supplied by DuPont: LUXPRINT™ type 7138J, a white phosphor; LUXPRINT™ type 7151J, a green-blue phosphor; and LUXPRINT™ type 7174J, a yellow-green phosphor; and ELECTRODAG™ EL-035A supplied by Acheson.

According to a sixth embodiment of the electroluminescent device, according to the present invention, the electroluminescent device further comprises a layer of an electroluminescent phosphor, wherein the electroluminescent phosphor is a zinc sulphide phosphor doped with manganese and encapsulated with AlN.

According to a seventh embodiment of the electroluminescent device, according to the present invention, the electroluminescent device further comprises a dielectric layer.

Any dielectric material may be used in the dielectric layer, 5 with yttria and barium titanate being preferred e.g. the barium titanate paste LUXPRINT™ type 7153E high K dielectric insulator supplied by DuPont and the barium titanate paste ELECTRODAG™ EL-040 supplied by Acheson. A positive ion exchanger may be incorporated into the dielectric layer to capture any ions dissolving escaping 10 from the phosphor of the light-emitting layer. The amount of ion exchanger in the dielectric layer has to be optimized so that it has a maximum effectiveness in reducing black spots while not reducing the initial brightness level. It is therefore preferred to add 0.5 to 50 parts by weight of ion exchanger to 100 parts by 15 weight of the total amount of resin and dielectric material in the dielectric layer. The ion exchanger may be organic or inorganic.

Suitable inorganic ion exchangers are hydrated antimony pentoxide powder, titanium phosphate, salts of phosphoric acid and silicic acid and zeolite.

20 Aspects of the present invention are also realized by a light emitting diode comprising the above-described conductive layer or produced according to the above-described process.

According to a first embodiment of the light-emitting diode, according to the present invention, the light-emitting diode 25 further comprises a electroluminescent layer comprising a low molecular weight electroluminescent compound.

According to a second embodiment of the light-emitting diode, according to the present invention, the light-emitting diode further comprises a electroluminescent layer comprising a polymeric 30 electroluminescent compound.

According to a third embodiment of the light-emitting diode, according to the present invention, the light-emitting diode further comprises electroluminescent quantum dots.

35

Photovoltaic devices

Aspects of the present invention are also realized by a photovoltaic device comprising the conductive layer, according to the present invention, or produced according to the process, 40 according to the present invention.

Aspects of the present invention are also realized by a solar cell comprising the conductive layer, according to the present

invention, or produced according to the process, according to the present invention.

According to a first embodiment of the photovoltaic device, according to the present invention, the photovoltaic device further comprises at least one photovoltaic layer. The photovoltaic layer may be organic layer, a hybrid inorganic and organic layer or an inorganic layer.

Photovoltaic devices incorporating the conductive layer, according to the present invention, can be of two types: the regenerative type which converts light into electrical power leaving no net chemical change behind in which current-carrying electrons are transported to the anode and the external circuit and the holes are transported to the cathode where they are oxidized by the electrons from the external circuit and the photosynthetic type in which there are two redox systems one reacting with the holes at the surface of the semiconductor electrode and one reacting with the electrons entering the counter-electrode, for example, water is oxidized to oxygen at the semiconductor photoanode and reduced to hydrogen at the cathode. In the case of the regenerative type of photovoltaic cell, as exemplified by the Graetzel cell, the electron transporting medium may be a nano-porous metal oxide semiconductor with a band-gap of greater than 2.9 eV, such as titanium dioxide, niobium(V) oxide, tantalum(V) oxide and zinc oxide, the hole transporting medium may be a liquid electrolyte supporting a redox reaction, a gel electrolyte supporting a redox reaction, an organic hole transporting material, which may be a low molecular weight material such as 2,2',7,7'-tetrakis(N,N-di-p-methoxyphenyl-amine)9,9'-spirobifluorene (OMeTAD) or triphenylamine compounds or a polymer such as PPV-derivatives, poly(N-vinylcarbazole) etc., or inorganic semiconductors such as CuI, CuSCN etc. The charge transporting process can be ionic as in the case of a liquid electrolyte or gel electrolyte or electronic as in the case of organic or inorganic hole transporting materials.

Such regenerative photovoltaic devices can have a variety of internal structures in conformity with the end use. Conceivable forms are roughly divided into two types: structures which receive light from both sides and those which receive light from one side. An example of the former is a structure made up of a transparently conductive layer e.g. an ITO-layer or a PEDOT/PSS-containing layer and a transparent counter electrode electrically conductive layer e.g. an ITO-layer or a PEDOT/PSS-containing layer having interposed therebetween a photosensitive layer and a charge transporting

layer. Such devices preferably have their sides sealed with a polymer, an adhesive or other means to prevent deterioration or volatilization of the inside substances. The external circuit connected to the electrically-conductive substrate and the counter
5 electrode via the respective leads is well-known.

Alternatively the spectrally sensitized nano-porous metal oxide, according to the present invention, can be incorporated in hybrid photovoltaic compositions such as described in 1991 by Graetzel et al. in Nature, volume 353, pages 737-740, in 1998 by U.
10 Bach et al. [see Nature, volume 395, pages 583-585 (1998)] and in 2002 by W. U. Huynh et al. [see Science, volume 295, pages 2425-2427 (2002)]. In all these cases, at least one of the components (light absorber, electron transporter or hole transporter) is inorganic (e.g. nano-TiO₂ as electron transporter, CdSe as light
15 absorber and electron transporter) and at least one of the components is organic (e.g. triphenylamine as hole transporter or poly(3-hexylthiophene) as hole transporter).

Transistors

20

Aspects of the present invention are also realized by a transistor comprising the conductive layer, according to the present invention, or produced according to the process, according to the present invention.

25

According to a first embodiment of the transistor, according to the present invention, the transistor further comprises a layer with one or more of the electron transporting or hole transporting components described above, but within such a configuration that it can be used as a transistor. The semiconductor can be n-type, p-
30 type or both (ambipolar transistor) and can be either organic or inorganic.

Industrial application

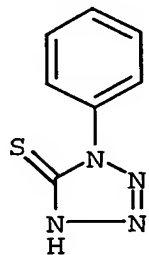
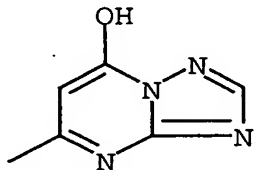
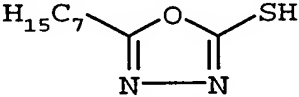
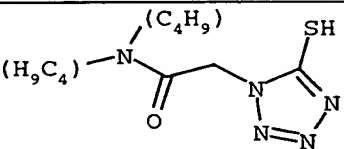
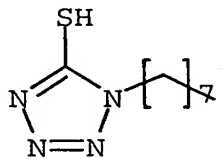
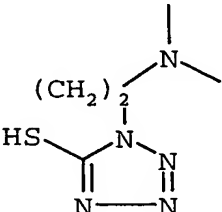
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A conductive layer, according to the present invention, can be used in a wide range of electronic devices such as photovoltaic devices, solar cells, batteries, capacitors, light emitting diodes, organic and inorganic electroluminescent devices, smart windows, electrochromic devices, sensors for organic and bio-organic
40 materials and field effect transistors [see also chapter 10 of the Handbook of Oligo- and Polythiophenes, Edited by D. Fichou, Wiley-VCH, Weinheim (1999)].

The invention is illustrated hereinafter by way of INVENTION and COMPARATIVE EXAMPLES. The percentages and ratios given in these examples are by weight unless otherwise indicated.

5

Ingredients used in the comparative experiments of EXAMPLE 2:

	Structural formula	
STAB01		1-phenyl-5-mercapto-tetrazole
STAB02		sodium tartrate
STAB03		thiourea
STAB04	Na ₂ S	sodium sulphide
STAB05		5-methyl-s-triazolo[1,5-a]pyrimidin-7-ol
STAB06		
STAB07		
STAB08	<p>Na⁺</p> 	
STAB09		

EXAMPLE 1 (COMPARATIVE)

Conductive Ag-pattern made by Diffusion Transfer Reaction with
conductive PEDOT/PSS on top

5

Preparation of Material A:

The preparation of the physical development nuclei (PdS) is described in the example of EP-A 0769 723. From this example
10 solutions A1, B1 and C1 were used to prepare the nuclei. To 1000 ml of this PdS dispersion 10 g of a 10 g/L water solution of Aerosol OT from American Cyanamid and 5 g of a 50 g/L solution of perfluorocaprylamide-polyglycol were added. This dispersion was then coated to a wet layer thickness of 13.5 μm on a poly(ethylene
15 terephthalate) support with a 4 μm thick gelatine subbing layer and then dried for 60 minutes at 25°C. This is material A.

Preparation of the PEDOT/PSS dispersion:

20 EP-A 686662 and US 5,766,515 disclose in the example the preparation of a 1.2% PEDOT/PSS dispersion in water. 15 ml of a 2% solution of ZONYL™ FSO100 in water, 1.25 g of Z6040, a silane from DOW CORNING and 25 g of diethylene glycol were added to 106 g of this dispersion to give the PEDOT/PSS dispersion used in the
25 following EXAMPLES.

Preparation of Material B:

The above-described PEDOT/PSS dispersion was used to coat
30 Material A to a wet thickness of 40 μm and was then dried for 15 minutes at 100°C, thereby producing material C.

Preparation of the transfer emulsion layer:

35 The preparation of the silver chlorobromide emulsion and the preparation of the transfer emulsion layer was as disclosed in EP-A 769 723 except that the coverage of silver halide applied was equivalent to 1.25 g/m² of AgNO₃ instead of 2 g/m² thereof.

Exposure and development of Materials A and B:

The transfer emulsion layer was exposed image-wise as shown in Figure 1 and processed in contact with the receiver (Material A and material B) at 25°C for 10s with a AGFA-GEVAERT™ CP297 developer solution.

Preparation of the double layer electrode configuration:

10 Processed material A was coated with the above-described PEDOT/PSS-dispersion to a wet-layer thickness of 50 μm and then dried for 20 minutes at 120°C. The surface resistivity of the PEDOT/PSS layer was about 500 Ω/square in the non-exposed areas of material A. Material C was thereby prepared.

15 Evaluation of materials B and C:

The surface resistance measurements were carried out as follows: the layer electrode configurations were cut into strips 20 3.5 cm in width to ensure perfect positioning of the electrode material; parallel copper electrodes each 35 mm long, 3 mm wide and 35 mm apart, capable of forming line contacts and mounted on a TEFLON™ insulator were brought into contact with the outermost conductive layer of the strip giving a contacting area of 3.5 x 3.5 25 cm^2 , a constant contact force being ensured by placing a 4 kg weight on the TEFLON™ mounting; and the surface resistance was then directly measured using a Fluke-77 III Multimeter.

The optical density of the conductive layers was determined in transmission using a MacBeth™ TD924 densitometer with a visible 30 filter for conductive layers without photographic treatment, in pattern type (d) in which no silver was developed and in pattern (a) in which silver was developed over the whole 3 cm x 3 cm area without deducting the density of the support. The surface resistances and optical densities (complete material) after 35 exposure and development according to the patterns shown in Figure 1 are given in Table 1.

Table 1:

Control materials	Description	Pattern used from Fig 1		trans-mission O.D.	Surface resistance [Ω /square]
		type	description		
B	Without any photographic treatment	-	-	0.09	500
B	After transfer reaction	a	Solid area	2.30	5.2
B	After transfer reaction	b	1 mm lines, 10 mm spacing	0.33*	37
B	After transfer reaction	c	150 μ m lines, 5 mm spacing	0.19*	165
B	After transfer reaction	d	No Ag developed	0.07	800
C	Without any photographic treatment	-	-	0.10	650
C	After transfer reaction	a	Solid area	2.50	2.3
C	After transfer reaction	b	1 mm lines, 10 mm spacing	0.35*	18
C	After transfer reaction	c	150 μ m lines, 5 mm spacing	0.20*	120
C	After transfer reaction	d	No Ag developed	0.09	750

* calculated values

5

EXAMPLE 2 (INVENTION)

Preparation of the palladium sulphide dispersion:

The preparation of the physical development nuclei (PdS) is described in the example of EP-A 0769 723. From this example solutions A1, B1 and C1 were used to prepare the nuclei.

Preparation of Material D:

100 g of the above-described PEDOT/PSS dispersion was mixed with 3.35 g of the PdS-dispersion. To this mixture, 1.25 g of a 10 g/L water solution of AEROSOL™ OT (American Cyanamid), 0.625 g of a 50 g/l solution of perfluorocaprylamidpolyglycol and 61.9 ml of water were added to give the coating dispersion. This dispersion was coated on a support consisting of a poly(ethylene terephthalate) film and a 4 μ m thick gelatin subbing layer to a wet-layer thickness of 50 μ m with a doctor blade and then dried for 15 minutes at 100°C to produce Material D.

Preparation of the transfer emulsion layer:

The preparation of the silver chlorobromide emulsion and the preparation of the transfer emulsion layer was as disclosed in EP-A 5 769 723 except that the coverage of silver halide applied was equivalent to 1.25 g/m^2 of AgNO_3 instead of 2 g/m^2 thereof.

exposure and development

10 The transfer emulsion layer was exposed image-wise as shown in Figure 1 and processed in contact with the receiver at 25°C for 10s with an AGFA-GEVAERT™ CP297 developer solution.

evaluation

15

Surface resistance and optical density measurements were carried out as described above for COMPARATIVE EXAMPLE 1 and the results are given in Table 2.

Comparing Tables 1 and 2, it is surprising that the surface 20 resistances and optical densities determined with the single layer composite material of the present invention of Material D are fully comparable with the two layer configuration of Material B with the same components produced using the same techniques and exhibited higher visible light transmission than the two layer configuration 25 of Material C in which the PEDOT/PSS-layer was coated on a non-continuous developed silver layer.

The embedding of the developed silver in the PEDOT/PSS-layer results is a greater flatness of the outermost surface of the single layer compared with the two layer configuration.

30 From Table 2 it can be concluded that (1) it is possible to expose the PEDOT/PSS layer to the AGFA-GEVAERT™ CP297 developer with minor loss in surface conductivity without affecting the optical transparency and (2) the silver-lines increase the "apparent" surface conductivity significantly as is the case with 35 two layer configurations with the same components indicating that the embedded developed silver forms of itself a conductive entity.

Table 2:

Invention material	Description	Pattern used from Fig 1		trans-mission O.D.	Surface resistance [Ω /square]
		type	description		
D	Without any photographic treatment	-	-	0.11	340
D	After transfer reaction	a	Solid area	2.04	7.2
D	After transfer reaction	b	1 mm lines, 10 mm spacing	0.28*	40
D	After transfer reaction	c	150 μ m lines, 5 mm spacing	0.16*	140
D	After transfer reaction	d	No Ag deposit	0.10	530

* calculated value

5

EXAMPLE 3 (INVENTION)

Conceptual experiments were carried out with a recorder film with a gelatine to silver ratio of 0.014. Exposed areas of 1 x 3 cm² as electrodes with a separation of 40 μ m gave conducting silver patterns upon processing by conventional graphic processing. The resulting electrode pattern had a surface resistance of 50 to 100 ohm/square.

These electrodes were conditioned for 3 days at 35°C and a relative humidity of 80%. The aqueous solutions used for treating the electrodes prior to applying a potential of 100 V between neighbouring electrodes are listed in Table 3.

Table 3:

Solution nr.		Solution		
		active ingredient	conc. (%)	solvent
1	3777150	STAB01 (1-phenyl-5-mercapto-tetrazole)	1.0	water*
2	3777151	STAB01	0.1	water*
3	3777152	STAB01 + Antarox™ CO 630#	1.0 + 0.5	water
4	3777153	STAB01 + Antarox™ CO 630#	0.1 + 0.5	water
5	3777154	STAB02 (sodium tartrate)	10	water
6	3777155	STAB02 (sodium tartrate)	1	water
7	3777156	STAB03 (thiourea)	10	water
8	3777157	STAB03 (thiourea)	1	water
9	3777158	STAB04 (sodium sulphide)	10	water

10	3777159	STAB04 (sodium sulphide)	1	water
11	3777166	STAB05 (5-methyl-s-triazolo[1,5-a]pyrimidin-7-ol)	4.25	water
12	3777167	STAB05	0.425	water
13	3777168	STAB05	1.7×10^{-2}	water
14	3777169	STAB05	1.7×10^{-4}	water
15	3777170	STAB05	1.7×10^{-5}	water
16	3777171	STAB05	1.7×10^{-6}	water
17	3780150	STAB06	0.5	water
18	3780151	STAB06	0.05	water
19	3780152	STAB06	0.005	water
20	3780153	STAB07	0.5	water
21	3780154	STAB07	0.05	water
22	3780155	STAB07	0.005	water
23	3780156	STAB08	0.5	water
24	3780157	STAB08	0.05	water
25	3780158	STAB08	0.005	water
26	3780159	STAB09	0.5	water
27	3780160	STAB09	0.05	water
28	3780161	STAB09	0.005	water
29	3777161	PMT01	0.1	ethanol
30	3777172	PMT01	0.004	ethanol
31	3777173	PMT01	4×10^{-5}	ethanol
32	3777174	PMT01	4×10^{-6}	ethanol
33	3780162	PMT02	0.5	water
34	3780163	PMT02	0.05	water
35	3780164	PMT02	0.005	water
36	3780165	PMT03	0.5	water
37	3780166	PMT03	0.05	water
38	3780167	PMT03	0.005	water
39	3780168	PMT04	0.5	ethanol
40	3780169	PMT04	0.05	ethanol
41	3780170	PMT04	0.005	ethanol
42	3780171	PMT05	0.5	water
43	3780172	PMT05	0.05	water
44	3780173	PMT05	0.005	water
45	3780175	PMT06	0.05	water
46	3780176	PMT06	0.005	water
47	3780178	PMT07	0.05	water
48	3780179	PMT07	0.005	water
49	3780180	PMT08	0.5	water
50	3780181	PMT08	0.05	water
51	3780182	PMT08	0.005	water
52	3780183	PMT09	0.5	water
53	3780184	PMT09	0.05	water

54	3780185	PMT09	0.005	water
55	3780187	PMT10	0.5	water
56	3780188	PMT10	0.05	water
57	3780190	PMT11	0.05	water
58	3780191	PMT11	0.005	water
59	3780193	PMT12	0.05	water
60	3780194	PMT12	0.005	water
61	3780196	PMT13	0.05	water
62	3780197	PMT13	0.005	water
63	3780199	PMT14	0.05	water
64	3780200	PMT14	0.005	water

a nonyl-phenyl-oxy- polyethyleneglycol(EO 9.5), from GAF

After treatment of the electrodes by dipping in the solution for 1 minute at 25°C, a potential of 100 V was applied between 5 neighbouring electrodes for 20 minutes. The result was viewed under a microscope and recorded photographically. The gap between the electrodes without pretreatment and before applying a potential was determined to be $43.0 \pm 0.7 \mu\text{m}$. Tables 4 and 5 record the final gap width and general observations concerning silver dendrite 10 formation after particular pretreatments and the subsequent application of a potential of 100 V for 20 minutes for the comparative experiments with STAB01 to STAB09 and for the invention experiments with PMT01 to PMT14 respectively.

Table 4:

Comparative exper- iment nr.		sol- ution nr.	result of applying 100 V for 20 min. between electrodes	
			final width of gap [μm]	observations
1#	3777165	none	25.8 ± 1.0	front formation
2*	3777164	none	28.3 ± 1.0	front formation
3*	3780201	none	43.1 ± 1.2	dendrites, but no front formation
4	3777150	1	23.6 ± 1.8	front formation
5	3777151	2	21.5 ± 2.5	front formation
6	3777152	3	25.5 ± 2.9	front formation
7	3777153	4	41.8 ± 0.7	dendrite formation
8	3777154	5	35.5 ± 1.3	front formation but loss of electrode contact
9	3777155	6	33.6 ± 1.7	front formation
10	3777156	7	27.8 ± 1.9	front formation
11	3777157	8	26.2 ± 2.9	front formation
12	3777158	9	22.1 ± 4.1	front formation but loss of electrode contact
13	3777159	10	27.8 ± 2.7	front formation
14	3777166	11	30.4 ± 1.7	front formation
15	3777167	12	26.0 ± 1.2	front formation
16	3777168	13	21.8 ± 2.0	zones with front formation/ zones with dendrites but no front formation
17	3777169	14	23.5 ± 3.1 43.8 ± 0.7	zones with front formation/ zones with dendrites but no front formation
18	3777170	15	25.7 ± 2.1 42.4 ± 1.0	zones with front formation/ zones with dendrites but no front formation
19	3777171	16	22.6 ± 2.3	zones with front formation/ zones with dendrites but no front formation
20	3780150	17	28.6 ± 0.6	front formation
21	3780151	18	26.7 ± 0.6	front formation
22	3780152	19	43.2 ± 0.6	dendrites, but no front formation
23	3780153	20	23.4 ± 0.9	front formation
24	3780154	21	24.9 ± 1.1	front formation
25	3780155	22	24.6 ± 0.6	front formation
26	3780156	23	32.2 ± 2.3	front formation
27	3780157	24	43.3 ± 0.6	dendrites, but no front formation
28	3780158	25	42.4 ± 1.8	dendrites, but no front formation
29	3780159	26	42.7 ± 1.7	dendrites, but no front formation
30	3780160	27	43.1 ± 1.0	occasional dendrites
31	3780161	28	43.0 ± 0.4	occasional dendrites

neither conditioning nor solution pretreatment prior to application of 100 V DC

5 * no solution pretreatment between conditioning and application of 100 V DC

Table 5:

Invention exper- iment nr.		sol- ution nr.	result of applying 100 V for 20 min. between electrodes	
			final width of gap [μm]	observations
1	3777161	29	41.9 ± 0.7	almost no dendrite formation
2	3777172	30	42.4 ± 0.7	almost no dendrite formation
3	3777173	31	41.5 ± 0.4	almost no dendrite formation
4	3777174	32	41.4 ± 1.1	occasional dendrites
5	3780162	33	29.8 ± 0.4	front formation
6	3780163	34	29.4 ± 1.4	front formation
7	3780164	35	43.1 ± 0.3	dendrites, but no front formation
8	3780165	36	42.9 ± 0.4	occasional dendrites
9	3780166	37	42.6 ± 0.7	occasional dendrites
10	3780167	38	43.3 ± 0.75	dendrites, but no front formation
11	3780168	39	42.4 ± 0.8	almost no dendrite formation
12	3780169	40	43.4 ± 0.7	occasional dendrites
13	3780170	41	42.4 ± 1.0	dendrites, but no front formation
14	3780171	42	43.9 ± 0.8	dendrites, but no front formation
15	3780172	43	43.8 ± 0.6	almost no dendrite formation
16	3780173	44	44.2 ± 0.4	almost no dendrite formation
17	3780175	45	42.9 ± 0.7	dendrites, but no front formation
18	3780176	46	43.4 ± 0.7	almost no dendrite formation
19	3780178	47	43.5 ± 1.0	occasional dendrites
20	3780179	48	43.2 ± 0.9	occasional dendrites
21	3780180	49	25.4 ± 2.3	front formation
22	3780181	50	43.4 ± 0.8	occasional dendrites
23	3780182	51	43.7 ± 0.4	almost no dendrite formation
24	3780183	52	43.3 ± 0.7	dendrites, but no front formation
25	3780184	53	42.0 ± 0.8	occasional dendrites
26	3780185	54	43.9 ± 0.5	almost no dendrite formation
27	3780187	55	24.1 ± 4.0	front formation
28	3780188	56	42.9 ± 0.9	dendrites, but no front formation
29	3780190	57	25.6 ± 3.3	front formation
30	3780191	58	43.0 ± 0.5	occasional dendrites
31	3780193	59	23.4 ± 3.0	front formation
32	3780194	60	42.8 ± 0.4	almost no dendrite formation
33	3780196	61	42.2 ± 0.6	occasional dendrites
34	3780197	62	41.9 ± 1.2	occasional dendrites
35	3780199	63	26.1 ± 2.1	front formation
36	3780200	64	41.6 ± 1.1	occasional dendrites

5 These results show migration of silver ions upon conditioning for 3 days at 35°C and 80% relative humidity and subsequent

application of a potential of 100 V DC for 20 minutes in the absence of pretreatment (comparative experiments 2 and 3). A comparison of the results with comparative experiments 1 and 2 show that conditioning clearly promoted silver dendrite growth as
5 observed in actual devices.

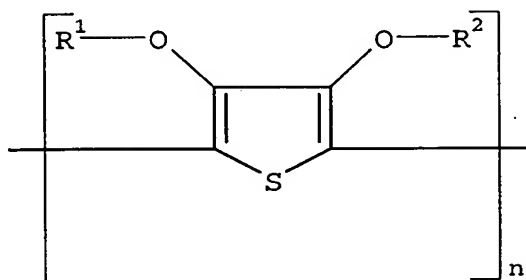
Pretreatment with an aqueous solution of sodium tartrate (STAB02) provided limited restraint as shown by the reduced growth of the silver dendrite front. Pretreatment with high concentrations of sodium sulphide (STAB04) appeared to detach the
10 silver dendrite front from the electrode. Low concentrations of 5-methyl-s-triazolo[1,5-a]pyrimidin-7-ol (STAB05) also restrained silver dendrite growth as evidenced by the break up of the silver dendrite front into clusters of silver dendrites although this was limited to particular zones.

15 All the 5-mercapto-tetrazoles investigated, with the notable exception of unsubstituted 1-phenyl-5-mercapto-tetrazole [STAB01], also exerted at least a limited restraint on the silver dendrite-formation process as could be seen by at least the appearance of a broken front formed by clusters of silver-dendrites. 1-phenyl-5-
20 mercapto-tetrazole itself exhibited this behaviour in the presence of the surfactant Antarox™ CO 630, a non-ionic surfactant. However, substantial restraint was only observed with 1-phenyl-mercapto-tetrazole compounds with the phenyl group substituted with at least one electron accepting group such as halide, acylamino or
25 amido groups as shown by the compounds PMT01 to PMT14. Almost complete restraint was observed upon pretreatment with solutions 29, 30, 31, 39, 43, 44, 46, 51, 54 and 60 i.e. with PMT1, PMT05, PMT06, PMT08, PMT09 and PMT12 almost complete restraint was observed at concentrations of 1-phenyl-5-mercapto-tetrazole with
30 phenyl groups substituted with electron accepting groups of 0.005% or lower.

The present invention may include any feature or combination of features disclosed herein either implicitly or explicitly or any
35 generalisation thereof irrespective of whether it relates to the presently claimed invention. In view of the foregoing description it will be evident to a person skilled in the art that various modifications may be made within the scope of the invention.

CLAIMS

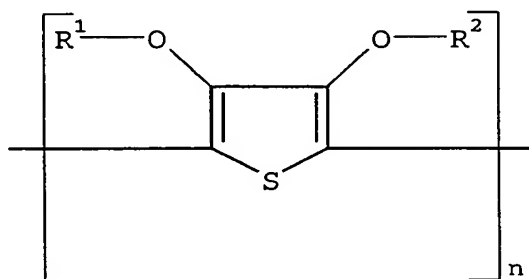
1. A substantially transparent conductive layer on a support,
said layer comprising an intrinsically conductive polymer and
a conductive metal non-uniformly distributed therein and
forming of itself a conductive entity.
2. Conductive layer according to claim 1, wherein said
intrinsically conductive polymer contains structural units
represented by formula (I):



(I)

- wherein n is larger than 1 and each of R^1 and R^2 independently represents hydrogen or an optionally substituted C_{1-4} alkyl group or together represent an optionally substituted C_{1-4} alkylene group or an optionally substituted cycloalkylene group, preferably an ethylene group, an optionally alkyl-substituted methylene group, an optionally C_{1-12} alkyl- or phenyl-substituted ethylene group, a 1,3-propylene group or a 1,2-cyclohexylene group.
3. Conductive layer according to claim 1, wherein said conductive metal is silver.
 4. Conductive layer according to claim 3, wherein said conductive layer further contains a 1-phenyl-5-mercato-tetrazole compound in which the phenyl group is substituted with one or more electron accepting groups.
 5. A process for preparing a substantially transparent conductive layer on a support, said layer comprising an intrinsically conductive polymer and a conductive metal non-uniformly distributed therein and forming of itself a conductive entity, comprising the step of: preparing said non-uniformly distributed conductive metal by a photographic process.

6. Process according to claim 5, wherein said photographic process comprises the steps of: coating the support with a layer containing said intrinsically conductive polymer and a nucleation agent; producing a non-continuous silver layer in said nucleation layer using silver salt diffusion transfer.
7. Process according to claim 6, wherein said nucleation agent is palladium sulphide.
8. Process according to claim 5, wherein said photographic process comprises the steps of: coating said support with a layer containing an intrinsically conductive polymer, silver halide and gelatin with a weight ratio of gelatin to silver halide in the range of 0.05 to 0.3, image-wise exposing said layer, and developing said exposed layer to produce said non-uniformly distributed silver.
9. Process according to claim 5, wherein said intrinsically conductive polymer contains structural units represented by formula (I):



(I)

- wherein n is larger than 1 and each of R¹ and R² independently represents hydrogen or an optionally substituted C₁₋₄ alkyl group or together represent an optionally substituted C₁₋₄ alkylene group or an optionally substituted cycloalkylene group, preferably an ethylene group, an optionally alkyl-substituted methylene group, an optionally C₁₋₁₂ alkyl- or phenyl-substituted ethylene group, a 1,3-propylene group or a 1,2-cyclohexylene group.
10. A light emitting diode comprising a substantially transparent conductive layer on a support, said layer comprising an intrinsically conductive polymer and a conductive metal non-

uniformly distributed therein and forming of itself a
conductive entity or prepared by a process for preparing a
substantially transparent conductive layer on a support, said
layer comprising an intrinsically conductive polymer and a
5 conductive metal non-uniformly distributed therein and forming
of itself a conductive entity, comprising the step of:
preparing said non-uniformly distributed conductive metal by a
photographic process.

10 11. A photovoltaic device comprising a substantially transparent
conductive layer on a support, said layer comprising an
intrinsically conductive polymer and a conductive metal non-
uniformly distributed therein and forming of itself a
conductive entity or prepared by a process for preparing a
15 substantially transparent conductive layer on a support, said
layer comprising an intrinsically conductive polymer and a
conductive metal non-uniformly distributed therein and forming
of itself a conductive entity, comprising the step of:
preparing said non-uniformly distributed conductive metal by a
20 photographic process.

12. A transistor comprising a substantially transparent conductive
layer on a support, said layer comprising an intrinsically
conductive polymer and a conductive metal non-uniformly
25 distributed therein and forming of itself a conductive entity
or prepared by a process for preparing a substantially
transparent conductive layer on a support, said layer
comprising an intrinsically conductive polymer and a
conductive metal non-uniformly distributed therein and forming
30 of itself a conductive entity, comprising the step of:
preparing said non-uniformly distributed conductive metal by a
photographic process.

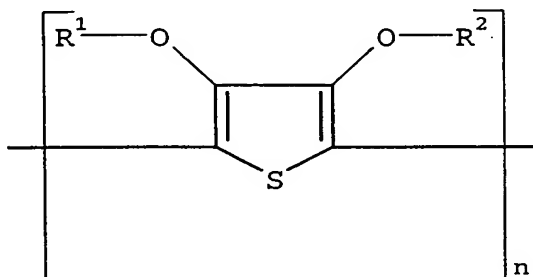
13. An electroluminescent device comprising a substantially
35 transparent conductive layer on a support, said layer
comprising an intrinsically conductive polymer and a
conductive metal non-uniformly distributed therein and forming
of itself a conductive entity or prepared by a process for
preparing a substantially transparent conductive layer on a
40 support, said layer comprising an intrinsically conductive
polymer and a conductive metal non-uniformly distributed
therein and forming of itself a conductive entity, comprising

the step of: preparing said non-uniformly distributed
conductive metal by a photographic process.

ABSTRACT

PROCESS FOR PREPARING A SUBSTANTIALLY TRANSPARENT CONDUCTIVE LAYER

A substantially transparent conductive layer on a support, the
5 layer comprising an intrinsically conductive polymer e.g.
containing an intrinsically conductive polymer optionally
containing structural units represented by formula (I):



10 wherein n is larger than 1 and each of R¹ and R² independently
represents hydrogen or an optionally substituted C₁₋₄ alkyl group or
together represent an optionally substituted C₁₋₄ alkylene group or
an optionally substituted cycloalkylene group, preferably an
ethylene group, an optionally alkyl-substituted methylene group, an
15 optionally C₁₋₁₂ alkyl- or phenyl-substituted ethylene group, a 1,3-
propylene group or a 1,2-cyclohexylene group; and a conductive
metal non-uniformly distributed therein and forming of itself a
conductive entity; a process for preparing the transparently
conductive layer; and light emitting diodes, photovoltaic devices,
20 transistors and electroluminescent devices comprising the above-
described conductive layer.

Figure 1:

